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## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 09-301046

(71)Applicant : ASAHI GLASS CO LTD

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## (54) SOLID POLYELECTROLYTE TYPE METHANOL FUEL CELL

## (57)Abstract:

PROBLEM TO BE SOLVED: To reduce a cross leak quantity, even if methanol is supplied through a gas phase and obtain a stable high output voltage by supporting a negative ion-exchanger by a porous membrane consisting of polyolefin or polyfluoro-olefin, and providing the obtained negative ion-exchange membrane as an electrolyte.

SOLUTION: A negative ion exchanger is supported by a porous membrane consisting of a fiber cloth made of polyolefin or polyfluoro-olefin such as PP, polytetrafluoroethylene or the like. This negative ion exchanger is preferably 1.0 to 3.0 milli equivalent per g of dry negative ion exchanger, and for example, the negative ion exchange group introduced into (chloromethyl) styrene/ divinylbenzene copolymer or 4-vinylpyridine/divinylbenzene copolymer is employed. This negative ion-exchange membrane with superior heat resistance and alkaline resistive properties is employed as an electrolyte for a solid poly electrolyte methanol fuel cell, and thereby gas-phase supply of methanol is made possible.

## LEGAL STATUS

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**CLAIMS**


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[Claim(s)]

[Claim 1] The solid-state polyelectrolyte type methanol fuel cell characterized by being the anion exchange membrane by which the anion exchanger was supported by the porous layer with which an electrolyte consists of a polyolefine or a poly-fluoro olefin.

[Claim 2] The solid-state polyelectrolyte type methanol fuel cell according to claim 1 whose ion exchange capacity of an anion exchanger is per [ 1.0 ] 1g of xeransis anion exchangers, - 3.0 milliequivalents.

[Claim 3] The solid-state polyelectrolyte type methanol fuel cell according to claim 1 or 2 which is the textile fabrics with which a porous layer consists of polypropylene, a polytetrafluoroethylene, ethylene / a tetrafluoroethylene copolymer, or a tetrafluoroethylene / hexafluoropropylene copolymer.

[Claim 4] The solid-state polyelectrolyte type methanol fuel cell according to claim 1, 2, or 3 whose anion exchanger is an anion exchanger by which it comes to introduce an anion-exchange machine into styrene (\*\*\*\*\* methyl) / divinylbenzene copolymer, or 4-vinylpyridine / divinylbenzene copolymer.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to a solid-state polyelectrolyte type methanol fuel cell.

[0002]

[Description of the Prior Art] home use since a propellant tends to deal with the methanol fuel cell which uses a methanol as a direct propellant and it is cheap, and industrial use -- it is comparatively expected as power of a small output scale

[0003] The theoretical output voltage of a methanol-oxygen fuel cell is the 1.2V [almost same] (25 degrees C) as the thing of a hydrogen fuel, and can expect the same property theoretically. For this reason, sufficient property is not acquired although much researches are made about the anodic oxidation reaction of a methanol.

[0004] Since that the oxidation catalyst of a methanol which has sufficient activity as this ground is not yet found out, and the ion exchange membrane usually used as an electrolyte have very high methanol permeability, the use luminous efficacy of a methanol is low, and in order that the methanol which reached the air pole which is a counter electrode may react on an air pole front face, an overvoltage increases, and it is mentioned that output voltage declines etc.

[0005] Although the technique of supplying a methanol by the gaseous phase and lowering the methanol concentration by the side of a membranous anode was reported while reaction temperature was set as 100 degrees C or more and the reaction rate of a methanol pole, and an air pole was gathered as the technique of solving the above-mentioned trouble using the electrode-layer zygote using the perfluoro carbon polymerization body membrane which has a sulfonic group, sufficient property was not acquired in the above-mentioned technique.

[0006] Moreover, when the ion exchange membrane which is an electrolyte is a cation exchange membrane, polarization increase of an air pole is also remarkable by increase of the overvoltage by increase of the amount of cross leakages of the methanol by the so-called cross leakage phenomenon in which the supplied methanol does not react on the methanol pole, but reaches an air pole as it is through an electrolyte, and an air pole being the acid ambient atmosphere.

[0007] Although the method of decreasing the amount of cross leakages of a methanol by using an anion exchange membrane instead of a cation exchange membrane, and moving an anion to an anode from a cathode as a means to solve the above-mentioned trouble is also considered, since the conventional anion exchange membrane does not have enough thermal resistance, in this technique, it has troubles, like that an output cannot be made high and alkali resistance is inadequate.

[0008]

[Problem(s) to be Solved by the Invention] It is in the purpose of this invention offering the methanol fuel cell of high power which used the anion exchange membrane excellent in thermal resistance and alkali resistance.

[0009]

[Means for Solving the Problem] The solid-state polyelectrolyte type methanol fuel cell characterized by this invention being the anion exchange membrane by which the anion exchanger was supported by the porous layer with which an electrolyte consists of a polyolefine or a polyfluoro olefin is offered.

[0010]

[Embodiments of the Invention] The methanol fuel cell of this invention is a solid-state

macromolecule type fuel cell which uses ion exchange membrane as electrolyte, and, typically, consists of the above-mentioned electrolyte and a gas diffusion electrode joined to both sides of the above-mentioned electrolyte.

[0011] The electrolyte which constitutes the methanol fuel cell of this invention is the anion exchange membrane by which the anion exchanger was supported by the porous layer which consists of a polyolefine or a poly-fluoro olefin.

[0012] As a porous layer, a polyolefine or a poly-fluoro olefin is used from thermal resistance and an alkali-proof viewpoint. Specifically, as a polyolefine, although polyethylene, polypropylene, etc. are illustrated, since especially thermal resistance is excellent, polypropylene is used preferably.

[0013] Moreover, as a poly-fluoro olefin, the polymer of the olefin which has one or more fluorine atoms can be used. Although a polytetrafluoroethylene (PTFE), a polychlorotrifluoroethylene resin, a polyvinylidene fluoride, ethylene / tetrafluoroethylene copolymer, a tetrafluoroethylene / hexafluoropropylene copolymer, etc. are specifically illustrated, especially PTFE, ethylene / tetrafluoroethylene copolymer, and a tetrafluoroethylene / hexafluoropropylene copolymer are desirable from thermal resistance and alkali resistance being excellent especially.

[0014] As for especially the thickness of a porous layer, it is desirable that it is 30-80 micrometers of  $\mu\text{s}$  5-200 micrometers from the viewpoint of an intensity, handling nature, and a membrane resistance. Moreover, although the current shield factor of a porous layer is as desirable as the parvus, it is especially specifically desirable that it is 20% or less of  $\mu\text{s}$  50% or less. Although not limited especially as gestalt of a porous layer, textile fabrics or a nonwoven fabric is used and especially  $\mu\text{s}$  is used preferably. Textile fabrics can also use the thing of how to weave any, such as plain weave, a twill weave, a satin, and a leno weave.

[0015] Moreover, as an electrolyte in this invention, the thing which comes to support an anion exchanger is used from the purpose which reduces the amount of cross leakages of a methanol. Specifically, the anion exchanger by which it comes to introduce an anion-exchange machine into styrene ( $\mu\text{s}$  methyl) / divinylbenzene copolymer, or the copolymer of 4-vinylpyridine / divinylbenzene is desirable. The above-mentioned ( $\mu\text{s}$  methyl) styrene may be any of o bodies, m bodies, p bodies, or such mixture. Moreover, the above-mentioned divinylbenzenes may also be any of o bodies, m bodies, p bodies, or such mixture. Since the copolymer which has a polymerization unit based on a divinylbenzene has a structure of cross linkage, it can enlarge the intensity of an anion exchanger.

[0016] An anion-exchange machine can be easily introduced by introducing the polymerization unit based on styrene ( $\mu\text{s}$  methyl), or the polymerization unit based on 4-vinylpyridine into the copolymer which has a polymerization unit based on a divinylbenzene.

[0017] The above-mentioned copolymer may contain the polymerization unit based on styrene, the polymerization unit based on 4-ethyl styrene, etc. from the purposes, such as a control of ion exchange capacity. When the above-mentioned copolymers are (( $\mu\text{s}$  methyl) styrene or 4-vinylpyridine) / divinylbenzene / styrene copolymer, the composition ratio of this polymer is a weight ratio, and it is desirable that it is : (styrene ( $\mu\text{s}$  methyl) or 4-vinylpyridine) divinylbenzene:styrene = 20-90:5-40:0-60. Since ion exchange capacity becomes small and a membrane resistance becomes large when the composition ratio of the polymerization unit based on styrene is larger than the above-mentioned domain, it is not desirable. Moreover, since a membrane resistance will increase and the parvus and a mechanical strength will fall if the composition ratio of the polymerization unit based on a divinylbenzene is larger than the above-mentioned domain, it is not desirable.

[0018] Moreover, as an anion-exchange machine introduced to the aforementioned polymer, what is strong-base nature is desirable, and, specifically, the 4th class ammonium or a pyridinium machine is used preferably. Moreover, when introducing the technique of carrying out fixed time immersing of the aforementioned polymer into the alcoholic solution of the 3rd amine when known technique can be used as the introductory technique of the anion-exchange machine to the aforementioned polymer and it introduces the polymerization unit based on a  $\mu\text{s}$  methyl styrene, and the polymerization unit based on 4-vinylpyridine, the technique immersed in a halogenated-hydrocarbon solvent in the aforementioned polymer is used.

[0019] the ion exchange capacity of an anion exchanger — per [ 1.0 ] 1g of xeransis anion exchangers — 3.0 milliequivalents, especially  $\mu\text{s}$  — 1.5 to 2.5 milliequivalent, it comes out and it is desirable that it is When ion exchange capacity is above-mentioned within the limits, a membrane resistance is low, and a layer intensity is large, and since the amount of methanol transparency

also decreases, it is desirable.

[0020] Although the technique of carrying out a polymerization etc. mentioned after infiltrating the technique and the monomer which coat an anion-exchanger polymer solution on a porous layer as technique of making an anion exchanger supporting, on a porous layer at a porous layer, in order to obtain the anion exchange membrane which has sufficient mechanical strength, after infiltrating a monomer into a porous layer, the technique of carrying out a polymerization is used preferably.

[0021] In addition, just the polymerization of a mechanical strength according [ monomers, such as a \*\*\*\*\* methyl styrene, 4-vinylpyridine, a divinylbenzene, or styrene, and the compatibility with those polymers ] to usual heating may be [ the polyolefine or poly-fluoro olefin which are used as a porous layer ] inadequate for a parvus reason. In this case, after irradiating an ionizing radiation in the status that the monomer was sunk in and carrying out the polymerization of the part to the technique of infiltrating a monomer and carrying out a polymerization, after performing ionizing-radiation irradiation processing of a gamma ray, an electron ray, etc. on a porous layer, or a porous layer, it is desirable to use the technique of carrying out the heating polymerization of the remainder etc.

[0022] As for especially the thickness of the anion exchange membrane manufactured as mentioned above, it is desirable that it is 30-80 micrometers of \*\*s 10-200 micrometers. The electrode used for the methanol fuel cell of this invention can be manufactured according to usual known technique. For example, it is desirable to hold the catalyst which gives the activity as a methanol pole or an air pole by hydrophobic resin binding material, such as PTFE, and to make it into the gas diffusion electrode of the shape of a sheet of the porous material field. Moreover, it can manufacture by technique, such as spraying of the distributed mixed liquor containing the material which constitutes a gas diffusion electrode, an application, and filtration.

[0023] What is conventionally known as a catalyst for electrodes can be used. For example, as a catalyst for methanol poles, alloy catalysts, such as a platinum catalyst, a platinum-ruthenium alloy, and a platinum-tin alloy, or the support catalyst which carried out distributed support of the particle of these catalysts on support, such as carbon, is mentioned. The platinum catalyst as a methanol pole with the same catalyst for air poles, a platinum-alloy system catalyst, a support catalyst, etc. are used.

[0024] Various technique, such as the technique of imprinting this to an anion exchange membrane, once forming an electrode in layers as the manufacture technique of the zygote of an electrode and an anion exchange membrane on base materials, such as the technique of forming a \*\* electrode directly on an anion exchange membrane and PTFE film, the technique of carrying out the hotpress of an electrode and the anion exchange membrane, and the technique of sticking with adhesion liquid and making it form, is applicable.

[0025]

[Function] It is thought that a move of the water and the methanol accompanied by the move of a proton which the electrolyte in this invention is an anion exchange membrane, and is considered to be generated when a cation exchange membrane is used, in order that an anion may move toward an anode from a cathode at the time of energization does not happen. Moreover, it is thought that they can reduce the permeability of a methanol from the case where it supplies with a liquid since the polyolefine and poly-fluoro olefin which are used as a porous layer are excellent in thermal resistance and can supply a methanol to a fuel cell cell with a gas. Furthermore, since the above-mentioned porous layer is excellent in alkali resistance, the overvoltage of an air pole becomes low, is stabilized and the voltage of high power is obtained.

[0026]

[Example] Hereafter, although an example (Example 1, Example 2) and the example (Example 3, Example 4) of a comparison explain this invention, this invention is not necessarily limited to these.

[0027] It is 2 the thickness of 60 micrometers, and the area of 1m under the <Example 1> room temperature and the nitrogen ambient atmosphere. 15kGy irradiation of the gamma ray was carried out at polypropylene textile fabrics (plain weave, 20% of current shield factors). The NBR rubber 10 weight section and the benzoyl-peroxide 2 weight section which is a polymerization initiator were added to the monomer mixed liquor of the styrene 25 weight section, the styrene (\*\*\*\*\* methyl) 55 weight section, and the divinylbenzene 20 weight section. After having sunk into the aforementioned textile fabrics, having made them support 50g of this mixed liquor and

performing graft polymerization at 25 degrees C for 24 hours, it was performed at 60 degrees C, and the polymerization was performed at 90 more degrees C for 3 hours for 10 hours. The obtained polymerization body membrane was flooded with the methanol solution of a trimethylamine with a concentration of one mol [ / l . ] at 40 degrees C for 36 hours, and the anion exchange membrane was obtained. In addition, the ion exchange capacity of the anion exchanger in this anion exchange membrane was 2.2 milliequivalents per 1g of xeransis anion exchangers.

[0028] The mixed liquor which added the NBR rubber 10 weight section and the benzoyl-peroxide 2 weight section for the textile fabrics (plain weave, 5% of current shield factors) of PTFE with a <Example 2> thickness of 50 micrometers into the monomer mixed liquor of the styrene 25 weight section, the 4-vinylpyridine 50 weight section, and the divinylbenzene 25 weight section was infiltrated. After having carried out 25kGy irradiation of the gamma ray and making this it carry out graft polymerization under a room temperature and the nitrogen ambient atmosphere, it was performed at 60 degrees C, and the heating polymerization was performed at 90 more degrees C for 3 hours for 10 hours, and the polymerization was completed. The obtained polymerization body membrane was flooded with the hexane solution (10 % of the weight of concentration) of a methyl iodide at 35 degrees C for 48 hours, and the anion exchange membrane was obtained. In addition, the ion exchange capacity of the anion exchanger in this anion exchange membrane was 2.4 milliequivalents per 1g of xeransis anion exchangers.

[0029] Instead of <Example 3> polypropylene, the anion exchange membrane was obtained like Example 1 except having used the textile fabrics (plain weave, 20% of current shield factors) of a polyvinyl chloride with a thickness of 80 micrometers.

[0030] As a <Example 4> electrolyte, perfluoro carbon sulfonic-acid ion exchange membrane (Du Pont product name:Nafion 117) was used.

[0031] As a [evaluation result] electrolyte, the anion exchange membrane produced in Example 1 and Example 2 was used. the platinum-rubidium alloy catalyst covered with the anion exchange resin which amine-izes the chloromethylation object of the copolymer of aromatic polyether sulphone and an aromatic poly thioether sulfone, and is obtained as an anode electrode -- the amount of platinum -- seeing -- per surface area -- 2mg/cm<sup>2</sup> it produces so that it may become -- having -- electrode effective area -- 10cm<sup>2</sup> it is -- the gas diffusion electrode was used the platinum catalyst covered with the above-mentioned anion exchange resin as a cathode electrode -- the amount of platinum -- seeing -- per surface area -- 1mg/cm<sup>2</sup> it produces so that it may become -- having -- electrode effective area -- 10cm<sup>2</sup> it is -- the cathode electrode was used for the gas diffusion electrode The above-mentioned anion exchange membrane, the anode electrode, and the cathode electrode were joined in the hot pressing, and the zygote of an electrode-layer was produced.

[0032] Moreover, as an electrolyte, the cation exchange membrane produced in the anion exchange membrane produced in Example 3 or Example 4 was used, and the zygote of an electrode-layer was produced like the above-mentioned process except having covered with the cation exchange resin of Nafion 117 and this composition the catalyst used for the anode electrode and the cathode electrode.

[0033] The obtained above-mentioned zygote was inserted between the separators with a rib of a couple, respectively, and the fuel cell cell was assembled. The air which is oxidizer gas was supplied to the fuel cell cell through the humidifier held at 130 degrees C, 20% of the weight of the methanol aqueous solution which is fuel gas was made to gasify through the vaporization room held at 140 degrees C, the fuel cell cell was supplied, and the power generation examination was carried out at the three normal atmosphere and the cell temperature of 130 degrees C. It is 2 the current density of 100mA/cm to Table 1. Output voltage is shown.

[0034]

[Table 1]

	出力電圧 (V)
例 1	0. 6 0
例 2	0. 6 1
例 3	0. 5 2
例 4	0. 5 0

[0035]

[Effect of the Invention] By making the porous layer of the polyolefine excellent in thermal resistance and alkali resistance, or a poly-fluoro olefin support an anion exchanger, gaseous-phase supply of a methanol is attained, the amount of cross leakages of a methanol is reduced, and the solid-state polyelectrolyte type methanol fuel cell from which it is stabilized and a high power voltage is obtained is obtained.

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Field

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[The technical field to which invention belongs] this invention relates to a solid-state  
polyelectrolyte type methanol fuel cell.

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Technique

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[0003] The theoretical output voltage of a methanol-oxygen fuel cell is the 1.2V [ almost same ] (25 degrees C) as the thing of a hydrogen fuel, and can expect the same property theoretically. For this reason, sufficient property is not acquired although much researches are made about the anodic oxidation reaction of a methanol.

[0004] Since that the oxidation catalyst of a methanol which has sufficient activity as this ground is not yet found out, and the ion exchange membrane usually used as an electrolyte have very high methanol permeability, the use luminous efficacy of a methanol is low, and in order that the methanol which reached the air pole which is a counter electrode may react on an air pole front face, an overvoltage increases, and it is mentioned that output voltage declines etc.

[0005] Although the technique of supplying a methanol by the gaseous phase and lowering the methanol concentration by the side of a membranous anode was reported while reaction temperature was set as 100 degrees C or more and the reaction rate of a methanol pole and an air pole was gathered as the technique of solving the above-mentioned trouble using the electrode-layer zygote using the perfluoro carbon polymerization body membrane which has a sulfonic group, sufficient property was not acquired in the above-mentioned technique.

[0006] Moreover, when the ion exchange membrane which is an electrolyte is a cation exchange membrane, polarization increase of an air pole is also remarkable by increase of the overvoltage by increase of the amount of cross leakages of the methanol by the so-called cross leakage phenomenon in which the supplied methanol does not react on the methanol pole, but reaches an air pole as it is through an electrolyte, and an air pole being the acid ambient atmosphere.

[0007] Although the method of decreasing the amount of cross leakages of a methanol by using an anion exchange membrane instead of a cation exchange membrane, and moving an anion to an anode from a cathode as a means to solve the above-mentioned trouble is also considered, since the conventional anion exchange membrane does not have enough thermal resistance, in this technique, it has troubles, like that an output cannot be made high and alkali resistance is inadequate.

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Effect

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[Effect of the Invention] By making the porous layer of the polyolefine excellent in thermal resistance and alkali resistance, or a poly-fluoro olefin support an anion exchanger, gaseous-phase supply of a methanol is attained, the amount of cross leakages of a methanol is reduced, and the solid-state polyelectrolyte type methanol fuel cell from which it is stabilized and a high power voltage is obtained is obtained.

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TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] It is in the purpose of this invention offering the methanol fuel cell of high power which used the anion exchange membrane excellent in thermal resistance and alkali resistance.

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**MEANS**


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[Means for Solving the Problem] The solid-state polyelectrolyte type methanol fuel cell characterized by this invention being the anion exchange membrane by which the anion exchanger was supported by the porous layer with which an electrolyte consists of a polyolefine or a poly-fluoro olefin is offered.

[0010]

[Embodiments of the Invention] The methanol fuel cell of this invention is a solid-state macromolecule type fuel cell which uses ion exchange membrane as an electrolyte, and, typically, consists of the above-mentioned electrolyte and a gas diffusion electrode joined to both sides of the above-mentioned electrolyte.

[0011] The electrolyte which constitutes the methanol fuel cell of this invention is the anion exchange membrane by which the anion exchanger was supported by the porous layer which consists of a polyolefine or a poly-fluoro olefin.

[0012] As a porous layer, a polyolefine or a poly-fluoro olefin is used from thermal resistance and an alkali-proof viewpoint. Specifically, as a polyolefine, although polyethylene, polypropylene, etc. are illustrated, since especially thermal resistance is excellent, polypropylene is used preferably.

[0013] Moreover, as a poly-fluoro olefin, the polymer of the olefin which has one or more fluorine atoms can be used. Although a polytetrafluoroethylene (PTFE), a polychlorotrifluoroethylene resin, a polyvinylidene fluoride, ethylene / tetrafluoroethylene copolymer, a tetrafluoroethylene / hexafluoropropylene copolymer, etc. are specifically illustrated, especially PTFE, ethylene / tetrafluoroethylene copolymer, and a tetrafluoroethylene / hexafluoropropylene copolymer are desirable from thermal resistance and alkali resistance being excellent especially.

[0014] As for especially the thickness of a porous layer, it is desirable that it is 30-80 micrometers of \*\*s 5-200 micrometers from the viewpoint of an intensity, handling nature, and a membrane resistance. Moreover, although the current shield factor of a porous layer is as desirable as the parvus, it is especially specifically desirable that it is 20% or less of \*\*s 50% or less. Although not limited especially as gestalt of a porous layer, textile fabrics or a nonwoven fabric is used and especially \*\*\*\*\* is used preferably. Textile fabrics can also use the thing of how to weave any, such as plain weave, a twill weave, a satin, and a leno weave.

[0015] Moreover, as an electrolyte in this invention, the thing which comes to support an anion exchanger is used from the purpose which reduces the amount of cross leakages of a methanol. Specifically, the anion exchanger by which it comes to introduce an anion-exchange machine into styrene (\*\*\*\*\* methyl) / divinylbenzene copolymer, or the copolymer of 4-vinylpyridine / divinylbenzene is desirable. The above-mentioned (\*\*\*\*\* methyl) styrene may be any of o bodies, m bodies, p bodies, or such mixture. Moreover, the above-mentioned divinylbenzenes may also be any of o bodies, m bodies, p bodies, or such mixture. Since the copolymer which has a polymerization unit based on a divinylbenzene has a structure of cross linkage, it can enlarge the intensity of an anion exchanger.

[0016] An anion-exchange machine can be easily introduced by introducing the polymerization unit based on styrene (\*\*\*\*\* methyl), or the polymerization unit based on 4-vinylpyridine into the copolymer which has a polymerization unit based on a divinylbenzene.

[0017] The above-mentioned copolymer may contain the polymerization unit based on styrene, the polymerization unit based on 4-ethyl styrene, etc. from the purposes, such as a control of ion exchange capacity. When the above-mentioned copolymers are ((\*\*\*\*\* methyl) styrene or 4-vinylpyridine) / divinylbenzene / styrene copolymer, the composition ratio of this polymer is a weight ratio, and it is desirable that it is : (styrene (\*\*\*\*\* methyl) or 4-vinylpyridine)

divinylbenzene:styrene =20-90-5-40:0-60. Since ion exchange capacity becomes small and a membrane resistance becomes large when the composition ratio of polymerization unit based on styrene is larger than the above-mentioned domain, it is not desirable. Moreover, since a membrane resistance will increase and the parvus and a mechanical strength will fall if the composition ratio of the polymerization unit based on a divinylbenzene is larger than the above-mentioned domain, it is not desirable.

[0018] Moreover, as an anion-exchange machine introduced to the aforementioned polymer, what is strong-base nature is desirable, and, specifically, the 4th class ammonium or a pyridinium machine is used preferably. Moreover, when introducing the technique of carrying out fixed time immersing of the aforementioned polymer into the alcoholic solution of the 3rd amine when known technique can be used as the introductory technique of the anion-exchange machine to the aforementioned polymer and it introduces the polymerization unit based on a \*\*\*\*\* methyl styrene, and the polymerization unit based on 4-vinylpyridine, the technique immersed in a halogenated-hydrocarbon solvent in the aforementioned polymer is used.

[0019] the ion exchange capacity of an anion exchanger — per [ 1.0 ] 1g of xeransis anion exchangers — 3.0 milliequivalents, especially \*\* — 1.5 to 2.5 milliequivalent, it comes out and it is desirable that it is When ion exchange capacity is above-mentioned within the limits, a membrane resistance is low, and a layer intensity is large, and since the amount of methanol transparency also decreases, it is desirable.

[0020] Although the technique of carrying out a polymerization etc. is mentioned after infiltrating the technique and the monomer which coat an anion-exchanger polymer solution on a porous layer as technique of making an anion exchanger supporting, on a porous layer at a porous layer, in order to obtain the anion exchange membrane which has sufficient mechanical strength, after infiltrating a monomer into a porous layer, the technique of carrying out a polymerization is used preferably.

[0021] In addition, just the polymerization of a mechanical strength according [ monomers, such as a \*\*\*\*\* methyl styrene, 4-vinylpyridine, a divinylbenzene, or styrene, and the compatibility with those polymers ] to usual heating may be [ the polyolefine or poly-fluoro olefin which are used as a porous layer ] inadequate for a parvus reason. In this case, after irradiating an ionizing radiation in the status that the monomer was sunk in and carrying out the polymerization of the part to the technique of infiltrating a monomer and carrying out a polymerization, after performing ionizing-radiation irradiation processing of a gamma ray, an electron ray, etc. on a porous layer, or a porous layer, it is desirable to use the technique of carrying out the heating polymerization of the remainder etc.

[0022] As for especially the thickness of the anion exchange membrane manufactured as mentioned above, it is desirable that it is 30-80 micrometers of \*\*s 10-200 micrometers. The electrode used for the methanol fuel cell of this invention can be manufactured according to usual known technique. For example, it is desirable to hold the catalyst which gives the activity as a methanol pole or an air pole by hydrophobic resin binding material, such as PTFE, and to make it into the gas diffusion electrode of the shape of a sheet of the porous material field. Moreover, it can manufacture by technique, such as spraying of the distributed mixed liquor containing the material which constitutes a gas diffusion electrode, an application, and filtration.

[0023] What is conventionally known as a catalyst for electrodes can be used. For example, as a catalyst for methanol poles, alloy catalysts, such as a platinum catalyst, a platinum-ruthenium alloy, and a platinum-tin alloy, or the support catalyst which carried out distributed support of the particle of these catalysts on support, such as carbon, is mentioned. The platinum catalyst as a methanol pole with the same catalyst for air poles, a platinum-alloy system catalyst, a support catalyst, etc. are used.

[0024] Various technique, such as the technique of imprinting this to an anion exchange membrane, once forming an electrode in layers as the manufacture technique of the zygote of an electrode and an anion exchange membrane on base materials, such as the technique of forming a \*\* electrode directly on an anion exchange membrane and PTFE film, the technique of carrying out the hotpress of an electrode and the anion exchange membrane, and the technique of sticking with adhesion liquid and making it form, is applicable.

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## OPERATION

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[Function] It is thought that a move of the water and the methanol accompanied by the move of a proton which the electrolyte in this invention is an anion exchange membrane, and is considered to be generated when a cation exchange membrane is used, in order that an anion may move toward an anode from a cathode at the time of energization does not happen. Moreover, it is thought that they can reduce the permeability of a methanol from the case where it supplies with a liquid since the polyolefine and poly-fluoro olefin which are used as a porous layer are excellent in thermal resistance and can supply a methanol to a fuel cell cell with a gas. Furthermore, since the above-mentioned porous layer is excellent in alkali resistance, the overvoltage of an air pole becomes low, is stabilized and the voltage of high power is obtained.

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[Translation done.]



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EXAMPLE

[Example] Hereafter, although an example (Example 1, Example 2) and the example (Example 3, Example 4) of a comparison explain this invention, this invention is not necessarily limited to these.

[0027] It is 2 the thickness of 60 micrometers, and the area of 1m under the <Example 1> room temperature and the nitrogen ambient atmosphere. 15kGy irradiation of the gamma ray was carried out at polypropylene textile fabrics (plain weave, 20% of current shield factors). The NBR rubber 10 weight section and the benzoyl-peroxide 2 weight section which is a polymerization initiator were added to the monomer mixed liquor of the styrene 25 weight section, the styrene (\*\*\*\*\* methyl) 55 weight section, and the divinylbenzene 20 weight section. After having sunk into the aforementioned textile fabrics, having made them support 50g of this mixed liquor and performing graft polymerization at 25 degrees C for 24 hours, it was performed at 60 degrees C, and the polymerization was performed at 90 more degrees C for 3 hours for 10 hours. The obtained polymerization body membrane was flooded with the methanol solution of a trimethylamine with a concentration of one mol [/l. ] at 40 degrees C for 36 hours, and the anion exchange membrane was obtained. In addition, the ion exchange capacity of the anion exchanger in this anion exchange membrane was 2.2 milliequivalents per 1g of xeraxis anion exchangers.

[0028] The mixed liquor which added the NBR rubber 10 weight section and the benzoyl-peroxide 2 weight section for the textile fabrics (plain weave, 5% of current shield factors) of PTFE with a <Example 2> thickness of 50 micrometers into the monomer mixed liquor of the styrene 25 weight section, the 4-vinylpyridine 50 weight section, and the divinylbenzene 25 weight section was infiltrated. After having carried out 25kGy irradiation of the gamma ray and making this it carry out graft polymerization under a room temperature and the nitrogen ambient atmosphere, it was performed at 60 degrees C, and the heating polymerization was performed at 90 more degrees C for 3 hours for 10 hours, and the polymerization was completed. The obtained polymerization body membrane was flooded with the hexane solution (10 % of the weight of concentration) of a methyl iodide at 35 degrees C for 48 hours, and the anion exchange membrane was obtained. In addition, the ion exchange capacity of the anion exchanger in this anion exchange membrane was 2.4 milliequivalents per 1g of xeraxis anion exchangers.

[0029] Instead of <Example 3> polypropylene, the anion exchange membrane was obtained like Example 1 except having used the textile fabrics (plain weave, 20% of current shield factors) of a polyvinyl chloride with a thickness of 80 micrometers.

[0030] As a <Example 4> electrolyte, perfluoro carbon sulfonic-acid ion exchange membrane (Du Pont product name: Nafion 117) was used.

[0031] As a [evaluation result] electrolyte, the anion exchange membrane produced in Example 1 and Example 2 was used. the platinum-rubidium alloy catalyst covered with the anion exchange resin which amine-izes the chloromethylation object of the copolymer of aromatic polyether sulphone and an aromatic poly thioether sulfone, and is obtained as an anode electrode — the amount of platinum — seeing — per surface area — 2mg/cm<sup>2</sup> it produces so that it may become — having — electrode effective area — 10cm<sup>2</sup> it is — the gas diffusion electrode was used the platinum catalyst covered with the above-mentioned anion exchange resin as a cathode electrode — the amount of platinum — seeing — per surface area — 1mg/cm<sup>2</sup> it produces so that it may become — having — electrode effective area — 10cm<sup>2</sup> it is — the cathode electrode was used for the gas diffusion electrode The above-mentioned anion exchange membrane, the anode electrode, and the cathode electrode were joined in the hot pressing, and the zygote of an electrode-layer was produced.

[0032] Moreover, as an electrolyte, the cation exchange membrane produced in the anion exchange membrane production Example 3 or Example 4 was used, and the zygote of an electrode-layer was produced like the above-mentioned process except having covered with the cation exchange resin of Nafion 117 and this composition the catalyst used for the anode electrode and the cathode electrode.

[0033] The obtained above-mentioned zygote was inserted between the separators with a rib of a couple, respectively, and the fuel cell cell was assembled. The air which is oxidizer gas was supplied to the fuel cell cell through the humidifier held at 130 degrees C, 20% of the weight of the methanol aqueous solution which is fuel gas was made to gasify through the vaporization room held at 140 degrees C, the fuel cell cell was supplied, and the power generation examination was carried out at the three normal atmosphere and the cell temperature of 130 degrees C. It is 2 the current density of 100mA/cm to Table 1. Output voltage is shown.

[0034]

[Table 1]

	出力電圧 (V)
例 1	0. 6 0
例 2	0. 6 1
例 3	0. 5 2
例 4	0. 5 0

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最終頁に続く

(54)【発明の名称】 固体高分子電解質型メタノール燃料電池

(57)【要約】

【課題】メタノールのクロスリーク量を低減した、高出力のメタノール燃料電池を提供する。

【解決手段】電解質が、ポリオレフィンまたはポリフルオロオレフィンからなる多孔性膜に、陰イオン交換体が支持された陰イオン交換膜である固体高分子電解質型メタノール燃料電池。

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## 【特許請求の範囲】

【請求項1】電解質が、ポリオレフィンまたはポリフルオロオレフィンからなる多孔性膜に、陰イオン交換体が支持された陰イオン交換膜であることを特徴とする固体高分子電解質型メタノール燃料電池。

【請求項2】陰イオン交換体のイオン交換容量が乾燥陰イオン交換体1gあたり1.0～3.0ミリ当量である請求項1記載の固体高分子電解質型メタノール燃料電池。

【請求項3】多孔性膜が、ポリプロピレン、ポリテトラフルオロエチレン、エチレン/テトラフルオロエチレン共重合体、またはテトラフルオロエチレン/ヘキサフルオロプロピレン共重合体からなる織布である請求項1または2記載の固体高分子電解質型メタノール燃料電池。

【請求項4】陰イオン交換体が、(クロロメチル)スチレン/ジビニルベンゼン共重合体または4-ビニルピリジン/ジビニルベンゼン共重合体に、陰イオン交換基が導入されてなる陰イオン交換体である請求項1、2または3記載の固体高分子電解質型メタノール燃料電池。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、固体高分子電解質型メタノール燃料電池に関する。

【0002】

【従来の技術】メタノールを直接燃料として使用するメタノール燃料電池は、燃料が取り扱いやすく、安価であることから家庭用や産業用の比較的小出力規模の電源として期待されている。

【0003】メタノール-酸素燃料電池の理論出力電圧は、水素燃料のものと同様1.2V(25℃)であり、原理的には同様の特性が期待できる。このためメタノールの陽極酸化反応については数多くの研究がなされているが、十分な特性が得られていない。

【0004】この理由としては、十分な活性を有するメタノールの酸化触媒がまだ見いだされていないこと、通常電解質として用いられるイオン交換膜はメタノール透過性が非常に高いため、メタノールの利用効率が低く、かつ対極である空気極に到達したメタノールが空気極表面で反応するため過電圧が増大し、出力電圧が低下することなどが挙げられる。

【0005】上記問題点を解決する方法として、スルホン酸基を有するパーフルオロカーボン重合体膜を用いた電極-膜接合体を用い、反応温度を100℃以上に設定し、メタノール極、空気極の反応速度を上げるとともに、メタノールを気相で供給し膜のアノード側のメタノール濃度を下げる方法が報告されているが、上記方法においても十分な特性は得られていなかった。

【0006】また、電解質であるイオン交換膜が陽イオン交換膜である場合は、供給したメタノールがメタノール極で反応せず、電解質を通してそのまま空気極に達す

る、いわゆるクロスリーク現象によるメタノールのクロスリーク量の増大、および空気極が酸性雰囲気であることによる過電圧の増大により、空気極の分極増大も顕著である。

【0007】上記問題点を解決する手段として、陽イオン交換膜の代わりに陰イオン交換膜を用い、アニオンをカソードからアノードへと移動させることでメタノールのクロスリーク量を減少させる方法も考えられるが、この方法においては、従来の陰イオン交換膜は耐熱性が充分でないため出力を高くできないこと、耐アルカリ性が不充分であることなどの問題点がある。

【0008】

【発明が解決しようとする課題】本発明の目的は、耐熱性および耐アルカリ性に優れた陰イオン交換膜を使用した、高出力のメタノール燃料電池を提供することにある。

【0009】

【課題を解決するための手段】本発明は、電解質が、ポリオレフィンまたはポリフルオロオレフィンからなる多孔性膜に、陰イオン交換体が支持された陰イオン交換膜であることを特徴とする固体高分子電解質型メタノール燃料電池を提供する。

【0010】

【発明の実施の形態】本発明のメタノール燃料電池は、イオン交換膜を電解質とする固体高分子型燃料電池であり、典型的には、上記電解質と、上記電解質の両面に接合されたガス拡散電極とからなる。

【0011】本発明のメタノール燃料電池を構成する電解質は、ポリオレフィンまたはポリフルオロオレフィンからなる多孔性膜に、陰イオン交換体が支持された陰イオン交換膜である。

【0012】多孔性膜としては、耐熱性、耐アルカリ性の観点から、ポリオレフィンまたはポリフルオロオレフィンが用いられる。具体的にはポリオレフィンとしては、ポリエチレン、ポリプロピレン等が例示されるが、耐熱性が特に優れることからポリプロピレンが好ましく用いられる。

【0013】また、ポリフルオロオレフィンとしては、フッ素原子を1個以上有するオレフィンの重合体を使用できる。具体的にはポリテトラフルオロエチレン(PTFE)やポリクロロトリフルオロエチレン、ポリフッ化ビニリデン、エチレン/テトラフルオロエチレン共重合体、テトラフルオロエチレン/ヘキサフルオロプロピレン共重合体などが例示されるが、なかでもPTFE、エチレン/テトラフルオロエチレン共重合体、テトラフルオロエチレン/ヘキサフルオロプロピレン共重合体は、耐熱性および耐アルカリ性が特に優れることから好ましい。

【0014】多孔性膜の厚みは、強度、取り扱い性および膜抵抗の観点から、5～200μm、特に30～8

0  $\mu$ mであるのが好ましい。また、多孔性膜の電流遮蔽率は、小さいほど好ましいが、具体的には50%以下、特に20%以下であるのが好ましい。多孔性膜の形態としては特に限定されないが、織布または不織布が用いられ、特に織布が好ましく用いられる。織布は平織、斜文織、朱子織、からみ織などいずれの織り方のものも使用できる。

【0015】また、本発明における電解質としては、メタノールのクロスリンク量を低減させる目的から、陰イオン交換体が支持されてなるものが用いられる。具体的には、(クロロメチル)スチレン/ジビニルベンゼン共重合体、または4-ビニルピリジン/ジビニルベンゼンの共重合体に、陰イオン交換基が導入されてなる陰イオン交換体が好ましい。上記(クロロメチル)スチレンは、o体、m体、p体、またはこれらの混合物のいずれであってもよい。また、上記ジビニルベンゼンもo体、m体、p体、またはこれらの混合物のいずれであってもよい。ジビニルベンゼンに基づく重合単位を有する共重合体は、架橋構造を有することから、陰イオン交換体の強度を大きくできる。

【0016】ジビニルベンゼンに基づく重合単位を有する共重合体に、(クロロメチル)スチレンに基づく重合単位、または4-ビニルピリジンに基づく重合単位を導入することにより、陰イオン交換基を容易に導入できる。

【0017】上記共重合体は、イオン交換容量の制御等の目的からスチレンに基づく重合単位、4-エチルスチレンに基づく重合単位などを含有していてもよい。上記共重合体が、((クロロメチル)スチレンまたは4-ビニルピリジン)/ジビニルベンゼン/スチレン共重合体であるとき、該重合体の組成比は重量比で、((クロロメチル)スチレンまたは4-ビニルピリジン):ジビニルベンゼン:スチレン=20~90:5~40:0~60であるのが好ましい。スチレンに基づく重合単位の組成比が上記範囲より大きい場合は、イオン交換容量が小さくなり膜抵抗が大きくなるので好ましくない。また、ジビニルベンゼンに基づく重合単位の組成比が上記範囲より大きいと膜抵抗が増大し、小さいと機械的強度が低下するので好ましくない。

【0018】また、前記重合体へ導入する陰イオン交換基としては、強塩基性であるものが好ましく、具体的には、4級アンモニウム基またはピリジニウム基が好ましく用いられる。また、前記重合体への陰イオン交換基の導入方法としては、既知の方法が使用でき、クロロメチルスチレンに基づく重合単位を導入する場合は、第3アミンのアルコール溶液中に前記重合体を一定時間浸漬する方法、4-ビニルピリジンに基づく重合単位を導入する場合はハロゲン化炭化水素溶剤に前記重合体を浸漬する方法などが用いられる。

【0019】陰イオン交換体のイオン交換容量は、乾燥

陰イオン交換体1gあたり1.0~3.0ミリ当量、特に1.5~2.5ミリ当量、であるのが好ましい。イオン交換容量が上記範囲内である場合は、膜抵抗が低く、かつ膜強度が大きく、メタノール透過量も少なくなるので好ましい。

【0020】多孔性膜上に陰イオン交換体を支持させる方法としては、陰イオン交換体ポリマー溶液を多孔性膜上にコーティングする方法、モノマーを多孔性膜に含浸させた後、重合させる方法などが挙げられるが、十分な機械的強度を有する陰イオン交換膜を得るためには、モノマーを多孔性膜に含浸させた後、重合させる方法が好ましく用いられる。

【0021】なお、多孔性膜として用いられるポリオレフィンやポリフルオロオレフィン、クロロメチルスチレン、4-ビニルピリジン、ジビニルベンゼンまたはスチレンなどのモノマーや、それらのポリマーとの親和性が小さいため、通常の加熱による重合のみでは機械的強度が不十分な場合がある。この場合は、多孔性膜に $\gamma$ 線や電子線などの電離性放射線照射処理を行った後、モノマーを含浸させて重合させる方法、または、多孔性膜にモノマーを含浸した状態で電離性放射線を照射して一部を重合させた後、残部を加熱重合させる方法などを用いるのが好ましい。

【0022】上記のようにして製造された陰イオン交換膜の厚みは、10~200  $\mu$ m、特に30~80  $\mu$ mであるのが好ましい。本発明のメタノール燃料電池に使用する電極は、通常の既知の手法にしたがって製造できる。たとえば、メタノール極または空気極としての活性を付与する触媒を、PTFEなどの疎水性樹脂結着材で保持し、多孔質体のシート状のガス拡散電極とすることが好ましい。また、ガス拡散電極を構成する材料を含む分散混合液の噴霧、塗布、ろ過などの方法により製造できる。

【0023】電極用の触媒としては従来より知られているものを使用できる。例えば、メタノール極用の触媒としては白金触媒、白金-ルテニウム合金、白金-スズ合金などの合金触媒、またはこれらの触媒の微粒子をカーボンなどの担体上に分散担持させた担持触媒などが挙げられる。空気極用の触媒は、メタノール極と同様の白金触媒、白金合金系触媒、担持触媒などが用いられる。

【0024】電極と陰イオン交換膜との接合体の製造方法としては、陰イオン交換膜上にガ電極を直接形成する方法、PTFEフィルムなどの基材上に一旦電極を層状に形成した後にこれを陰イオン交換膜に転写する方法、電極と陰イオン交換膜とをホットプレスする方法、接着液により密着して形成させる方法など種々の方法を適用できる。

【0025】

【作用】本発明における電解質は陰イオン交換膜であり、通電時にはカソードからアノードに向かってアニオ

ンが移動するため、陽イオン交換膜を使用したときに生じると考えられている、プロトンの移動に伴う水およびメタノールの移動が起こらないと考えられる。また、多孔性膜として用いるポリオレフィンやポリフルオロオレフィンは耐熱性に優れており、燃料電池セルにメタノールを気体で供給できるため、液体で供給する場合よりメタノールの透過性を低減できると考えられる。さらに上記多孔性膜は耐アルカリ性に優れるため、空気極の過電圧が低くなり、安定して高出力の電圧が得られる。

#### 【0026】

【実施例】以下、本発明を実施例（例1、例2）および比較例（例3、例4）により説明するが、本発明は必ずしもこれらに限定されない。

【0027】＜例1＞室温、窒素雰囲気下にて、厚さ60 $\mu$ m、面積1m<sup>2</sup>のポリプロピレン織布（平織、電流遮蔽率20%）に、 $\gamma$ 線を15kGy照射した。スチレン25重量部、（クロロメチル）スチレン55重量部、ジビニルベンゼン20重量部のモノマー混合液に、NBRゴム10重量部、重合開始剤である過酸化ベンゾイル2重量部を加えた。この混合液50gを前記織布に含浸、担持させて25℃にて24時間グラフト重合を行った後、60℃で10時間、さらに90℃で3時間重合を行った。得られた重合体膜を濃度1モル/リットルのトリメチルアミンのメタノール溶液に40℃で36時間浸漬し、陰イオン交換膜を得た。なお、この陰イオン交換膜における陰イオン交換体のイオン交換容量は、乾燥陰イオン交換体1gあたり2.2ミリ当量であった。

【0028】＜例2＞厚さ50 $\mu$ mのPTFEの織布（平織、電流遮蔽率5%）を、スチレン25重量部、4-ビニルピリジン50重量部、ジビニルベンゼン25重量部のモノマー混合液に、NBRゴム10重量部、過酸化ベンゾイル2重量部を添加した混合液を含浸させた。これに、室温、窒素雰囲気下にて、 $\gamma$ 線を25kGy照射してグラフト重合させた後、60℃で10時間、さらに90℃で3時間加熱重合を行い重合を完結させた。得られた重合体膜を、ヨウ化メチルのヘキサン溶液（濃度10重量%）に35℃にて48時間浸漬し、陰イオン交換膜を得た。なお、この陰イオン交換膜における陰イオン交換体のイオン交換容量は、乾燥陰イオン交換体1gあたり2.4ミリ当量であった。

【0029】＜例3＞ポリプロピレンの代わりに、厚さ80 $\mu$ mのポリ塩化ビニルの織布（平織、電流遮蔽率20%）を用いた以外は例1と同様にして陰イオン交換膜を得た。

【0030】＜例4＞電解質として、パーフルオロカーボンスルホン酸イオン交換膜（デュポン社製品名：ナフィオン117）を用いた。

【0031】【評価結果】電解質としては、例1、例2で作製した陰イオン交換膜を使用した。アノード電極としては、芳香族ポリエーテルスルホンと芳香族ポリチオエーテルスルホンとの共重合体のクロロメチル化物をアミン化して得られる陰イオン交換樹脂で被覆された白金-ルビジウム合金触媒が、白金量が見かけ表面積あたり2mg/cm<sup>2</sup>になるように作製され、電極有効面積が10cm<sup>2</sup>であるガス拡散電極を用いた。カソード電極としては、上記陰イオン交換樹脂で被覆された白金触媒が白金量が見かけ表面積あたり1mg/cm<sup>2</sup>となるように作製され、電極有効面積が10cm<sup>2</sup>であるガス拡散電極をカソード電極を用いた。ホットプレス法にて上記陰イオン交換膜、アノード電極、およびカソード電極を接合し、電極-膜の接合体を作製した。

【0032】また、電解質として、例3で作製した陰イオン交換膜または例4で作製した陽イオン交換膜を使用し、アノード電極およびカソード電極に用いた触媒をナフィオン117と同組成のカチオン交換樹脂にて被覆したものとした以外は、上記製法と同様にして、電極-膜の接合体を作製した。

【0033】得られた上記接合体を、それぞれ一対のリブ付きセパレータの間にはさんで、燃料電池セルを組み立てた。酸化剤ガスである空気を、130℃に保持した加湿器を介して燃料電池セルに供給し、燃料ガスである20重量%のメタノール水溶液を、140℃に保持した気化室を介してガス化させて燃料電池セルに供給し、3気圧、セル温度130℃にて発電試験を実施した。表1に電流密度100mA/cm<sup>2</sup>での出力電圧を示す。

#### 【0034】

【表1】

	出力電圧 (V)
例1	0.60
例2	0.61
例3	0.52
例4	0.50

#### 【0035】

【発明の効果】耐熱性および耐アルカリ性に優れたポリオレフィンまたはポリフルオロオレフィンの多孔性膜に、陰イオン交換体を支持させることにより、メタノールの気相供給が可能となり、メタノールのクロスリーク量が低減され、安定して高出力電圧が得られる固体高分子電解質型メタノール燃料電池が得られる。

フロントページの続き

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